Near Edge Structure in Electron Energy Loss Spectra of Chromium Trioxide Intercalalted into Graphite and Some Chromium Oxides (Commemoration Issue Dedicated to Professor Natsu Uyeda, on the Occasion of His Retirment)

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Near Edge Structure in Electron Energy Loss Spectra of Chromium Trioxide Intercalalted into Graphite and Some Chromium Oxides

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Inner-shell electron excitation spectra of a chromium trioxide intercalated graphite compound, K_2CrO_4 and Cr_2O_3 have been investigated by electron energy loss spectroscopy. Especially, fine structures of the chromium *L* and oxygen *K* edge spectra were interpreted in terms of a molecular orbital model. It was found that the local symmetry around the chromium ion and the oxidation state affected the near edge structures of the spectra and its energy position. It was revealed that the chromium ion in the GIC is tetrahedrally surrounded by four oxygen ions and partially reduced from the hexavalent ion, Cr (VI). This partial reduction of chromium ion was caused by the charge transfer from the graphite to the intercalant layers.

KEY WORDS: Electron energy loss spectroscopy/ Near edge structure/ Graphite intercalation compound/

I. INTRODUCTION

Electron energy loss spectroscopy (EELS) combined with transmission electron microscopy is a powerful method for the structural and elemental analyses of a small specimen area of the order of a micrometer or less in size[1]. A fine structure appearing near the core edge in energy loss spectrum, which is usually called ELNES (Energy Loss Near Edge Structure), is closely related both to the local geometrical symmetry around the excited atom and to the electronic structure of the specimen[2-5].

In the present paper the ELNES obtained from a chromium trioxide (CrO_3) in graphite intercalation compound (GIC) is measured and compared with the ELNES of K_2CrO_4 and Cr_2O_3. The several works on the chromium trioxide intercalated compound have been carried out[6-9]. In our previous work[9], it has been revealed that the in-plane structure of the intercalant layers is incommensurate with respect to the graphite lattice, and that each unit cell contains one $(CrO_3)_3$ and an acetic acid used as solvent for sample preparation.

Since CrO_3 is a strong acid, it is expected that CrO_3 oxidizes the graphite layers of the GIC and some amounts of charge transfer from graphite to intercalant layers[8]. The amount of charge transfer is an important quantity which governs the electronic properties of GIC. The purpose of this work is to investigate the local structure around the chromium atom in the GIC and the oxidation state on

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the basis of the ELNES of chromium *L*-edge and oxygen *K*-edge.

II. EXPERIMENTAL

The measurements of the EELS reported here were performed with a transmission electron microscope (JEM-100C) operating at 100 kV and the parallel electron energy loss spectrometer (Gatan model 666)[10]. The microcomputer (Anritsu Packet-IIe) controlled the spectrometer and collected the data[11].

Because the spectra were recorded in parallel, the collection time of data were reduced by about three orders of magnitude as compared with a serial detection system[10]. Moreover, such a great improvement of the detection efficiency of the parallel-EELS made it possible to measure the spectrum of the core-loss energy region with an energy resolution of 1 eV by desaturating the electron source of LaB_6-filament. Such an improvement in the energy resolution is desirable for the study of the ELNES.

In the present experiment the electron microscope was operated in the selected area diffraction mode. The spectrum was acquired from a probe size of about 3 μm in diameter with a current density of 0.16 A/cm^2 and an intergration time of 20 sec. The acceptance angle restricted by an entrance aperture to the spectrometer was approximately 2 mrad, which allows us to use the dipole selection rule to interpret the ELNES.

The intercalation of chromium trioxide, CrO_3, into graphite was performed by the reaction of CrO_3 and graphite in acetic acid solution. The detail of sample preparation has been described in our previous paper[9]. For the sample preparation of Cr_2O_3, the thin polycrystalline chromium film was first prepared on the cleaved (100) face of a KCl crystal by using the vapor deposition technique and then the chromium thin film was heated at 400°C in air. The Cr_2O_3-film was floated off in water and supported on a copper grid. The samples of K_2CrO_4 were ground to a fine particle and supported on a gold-coated microgrid.

III. RESULTS AND DISCUSSION

Before considering the detailed structure of ELNES, the spectrum measured from the GIC over a wide energy loss range is presented in Fig. 1, which shows the relative intensity of the different features in the spectrum. The intense peaks around 300 eV are due to the excitations of carbon 1*s* electrons and the weak features near 530 eV and 580 eV are attributed to the excitations of oxygen 1*s* and chromium 2*p* core electrons, respectively. The weakness of latter peaks is due to the low concentrations of oxygen or chromium atoms compared with that of carbon atoms in the present compound besides the difference of the scattering power. This spectrum was measured with the dispersion of 0.5 eV/ch (ch denotes the channel of the detector) to get a wide energy loss range. In order to study the fine structure of each edge the spectra of the carbon *K* edge and of the oxygen *K* and chromium *L* edges were recorded with the dispersion of 0.1 eV/ch and 0.3 eV/ch, respectively.

The ELNES of carbon *K* edge of the GIC is shown in Fig. 2. The energy

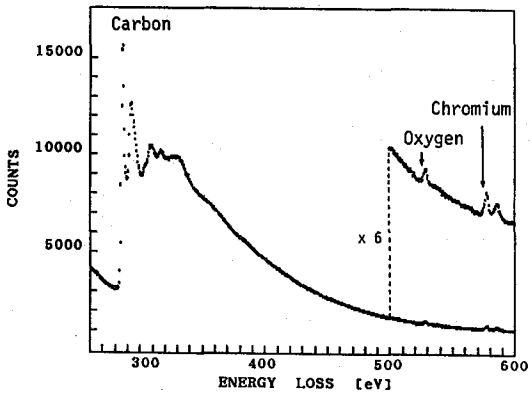

Fig. 1. Electron energy loss spectrum of chromium trioxide-GIC. The carbon K-edge is at 285 eV, the oxygen K-edge at 529 eV and the chromium L_2-edge at 578 eV.

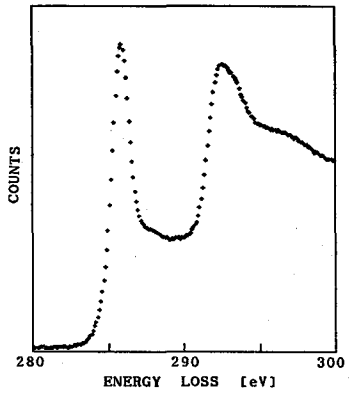

Fig. 2. The carbon K-shell excitation spectrum of chromium trioxide-GIC.

width of the 1s core levels is very narrow so that these fine structures directly reflect the density of state of the empty conduction band of the graphite. The ELNES agrees well with those from the pristine graphite except for the slight shift of the first peak at 285.9 eV by 0.1 eV to the higher energy region. This result indicates that the existence of intercalant layers in the GIC weakly perturbs the electronic structure of the graphite.

Since graphite is an anisotropic material, its band structure is well approximated by a two-dimensional band model. According to the calculation by Painter et al.[12], the first peak in the ELNES can be attributed to the transition from the 1s core state to the π^* antibonding band. The shift of 0.1 eV may be due to the increase in the binding energy of the carbon 1s electron of the GIC, because of the decrease of the net charge per carbon atom by the oxidation reaction[8]. Moreover, such a small chemical shift is related to the small number of oxidized graphite layers, because the present compound has the five stage structure[9]. Here, the stage number is defined as the number of graphite layers between the adjacent intercalant layers. Unfortunately, the further analysis based on this shift may be impossible, since the chemical shift of 0.1 eV is on the same order with the experimental uncertainty.

The ELNES of chromium $L_{2,3}$ edges measured from the GIC, K_2CrO_4 and Cr_2O_3 are shown in Fig. 3. The initial states associated with these loss peaks are chromium 2p core states which are originally splitted into $2p_{3/2}$ and $2p_{1/2}$ levels by the spin-orbit interaction. According to the dipole selection rule, the L_3 and L_2 edge structures are respectively attributed to the transitions from the $2p_{3/2}$ and $2p_{1/2}$ levels to unoccupied orbital having the d character.

At first sight the ELNES of the GIC is similar to that of K_2CrO_4 rather than Cr_2O_3. In both cases of the GIC and K_2CrO_4 the L_3 peak shows a further splitting into two peaks, a_1 and a_2, while no peak splitting in Cr_2O_3. Furthermore, the peak position of L_3 peak in Cr_2O_3 is lower than that of a_2 peak at the L_3 edge of K_2CrO_4 about 2.6 eV. The energy of these peak positions in ELNES of each compound

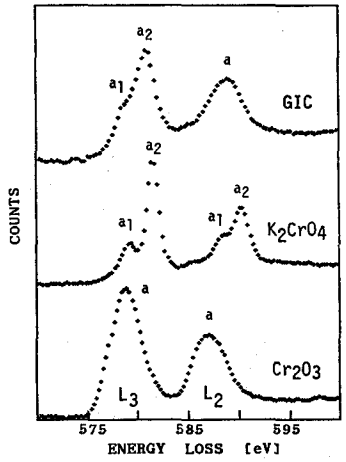

Fig. 3. The chromium $L_{2,3}$-shell excitation spectra of chromium trioxide-GIC, K_2CrO_4 and Cr_2O_3. The energies of the labelled peaks are given in Table 1.

are listed in Table 1.

Before considering the ELNES of the GIC, we start to interpret the ELNES of K_2CrO_4 and Cr_2O_3. As mentioned above, the fine structure and the peak position are related both to the local symmetry around the excited atom and to the electronic structure. In order to interpret the ELNES of transition metal oxides, the molecular orbital theory of the cluster representing the local structure around the excited atom has been applied[4,13,14]. In the present discussion we adopt the following molecular cluster model. In the K_2CrO_4 crystal each chromium ion (Cr^{6+}) is tetrahedrally surrounded by four oxygen atoms, while in the Cr_2O_3 crystal each chromium ion (Cr^{3+}) is octahedrally surrounded by six oxygen atoms. Thus, we use the $(CrO_4)^{2-}$ molecular cluster in the case of K_2CrO_4 and the $(CrO_6)^{9-}$ cluster in the case of Cr_2O_3.

The electronic structure of $(CrO_4)^{2-}$ cluster has been studied by Kutzler et al.[15] using the self-consistent multiple scattered wave $X\alpha$ method. According to their results, the two low unoccupied molecular orbitals are the lowest, doubly

Table 1. Energies (in eV) of the peaks in Figs. 3 and 5

			GIC	K_2CrO_4	Cr_2O_3
Chromium	L_3	a_1	578.9	579.4	
		a_2	581.1	581.6	
		a			579.0
	L_2	a_1		588.4	
		a_2		590.3	
		a	589.3		587.2
Oxygen K		a_1	529.6	529.8	
		a_2	531.1	531.1	
		a			532.5

degenerated e orbital and triply degenerated t_2 orbital, which are separated by 2.0 eV from each other. In the view point of crystal field theory, such a separation is interpreted that the 3*d* level of chromium ion is splitted by the electrostatic field with T_d-symmetry around the chromium ion. These orbitals are called crystal field orbitals which have mainly the chromium 3*d* character. Thus, the peak splitting into a_1 and a_2 at the L_3 or L_2 peak of K_2CrO_4 can be attributed to the transitions of 2*p* electrons to the e and t_2 crystal field orbitals, respectively. The energy separation between the peaks of a_1 and a_2 is 2.2 eV as shown in Table 1, which agrees well with the calculated value.

On the other hand, the molecular orbital of $(CrO_6)^{9-}$ cluster has been calculated by Tossell[16]. Since the $(CrO_6)^{9-}$ molecular cluster has the total spin ($S \neq 0$) at the ground state, the unrestricted self-consistent field calculation has been performed in his calculation in which the electrons having the up-spin and down-spin occupy different orbitals each other. He found that each highest occupied molecular orbitals of three $t_{2g}\uparrow$ is occupied by an up-spin electron, and low energy unoccupied molecular orbitals are $t_{2g}\downarrow$ and $e_g\uparrow$. The energy separation between $t_{2g}\uparrow$ and $e_g\uparrow$ orbitals is 2.3 eV, which can be also regarded as the crystal field splitting of chromium 3*d* level by the electrostatic field produced by oxygens arranged in O_h-symmetry. The energy of the $t_{2g}\downarrow$ orbital is 2.4 eV higher than the $t_{2g}\uparrow$ orbital because of the exchange interaction. Thus, the $t_{2g}\downarrow$ and $e_g\uparrow$ orbitals have alomst the same energy position. Therefore, the observed single peak of L_3 edge shown in Fig. 3 may be attributed to the transition from the $2p_{3/2}$ orbital to the $t_{2g}\downarrow$ and $e_g\uparrow$ orbitals.

From the above considerations, the splitting of the L_3 or L_2 peak constitutes an inherent feature of the tetrahedral coordination symmetry in the chromium oxide compounds. Since the crystal field splitting of 2.2 eV is observed in the L_3 peak of the GIC, it can be concluded that the chromium ion in the GIC is tetrahedrally surrounded by four oxygen atoms.

Further, the energy shift of the L_3 peak of Cr_2O_3 to lower region by 2.6 eV compared with the $L_3(a_2)$ peak of K_2CrO_4 is related to the net charge on a chromium ion in each compound. Because of the different oxidation state, the chromium ion of Cr (III) in Cr_2O_3 has more electrons than that of Cr (VI) ion in K_2CrO_4, so that the binding energy of chromium 2*p* core electron of Cr_2O_3 is smaller than that of K_2CrO_4. However, such a difference of the binding energy of core electrons dose not directly represents the energy shift of peak in the ELNES, because the relative energy positions of the final states of K_2CrO_4 and Cr_2O_3 are unknown.

The binding energy of a core electron can be measured directly by X-ray photoelectron spectroscopy (XPS). From the result of the XPS measurements on Cr_2O_3 and $K_2Cr_2O_7$ by Ikemoto et al.[17] the chemical shift of the peaks due to the ionization of 2*p* core electrons between Cr (III) and Cr (VI) ions is 3.0 eV. Since the chemical environments around the chromium ions in K_2CrO_4 and $K_2Cr_2O_7$ are almost identical, this value is assumed to be the energy difference between L_3 levels of K_2CrO_4 and Cr_2O_3. Then the $e_g\uparrow$ level of Cr_2O_3 is higher than the t_2 level of K_2CrO_4 by about 0.4 eV. The resultant energy level diagram is schematically

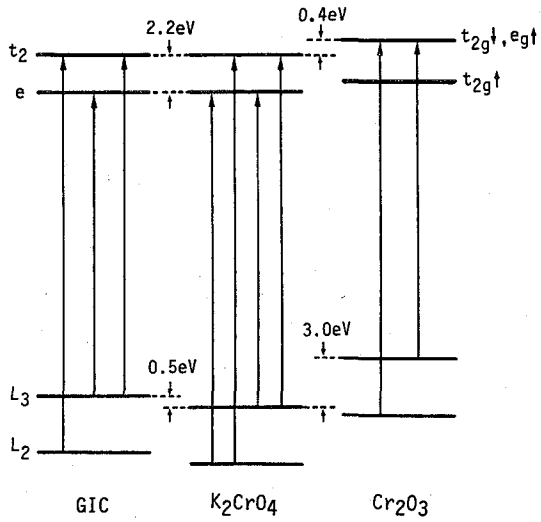

Fig. 4. The energy level diagram showing the transition observed in Fig. 3. The value of chemical shift between L_3 levels in K_2CrO_4 and Cr_2O_3 was taken from the XPS data (Ref. 17). Only the $t_{2g}\uparrow$ level of Cr_2O_3 is occupied by three electrons with up-spin and the other levels are empty at ground state.

drawn in Fig. 4 in which the arrows indicate the observed transitions in the present study.

It is noted that the a_2 peak at the L_3 edge of the GIC is shifted by -0.5 eV from the peak of K_2CrO_4 as shown in Table 1. Since the local structures around the chromium ion in the GIC and K_2CrO_4 are alomst equivalent, the t_2 levels of the GIC and K_2CrO_4 may be in the same energy position. Therefore, it can be interpreted that this energy difference is attributed to the smaller binding energy of $2p$ core electron of the chromium ion in the GIC. In other words, the L_3 level of Cr (VI) in the GIC is 0.5 eV higher than that in K_2CrO_4. It is generally said that the charge transfer from the graphite layers to the intercalant layers is the principal origin of the formation of the GIC. In the present case the transfered charge may partially occupy the lowest unoccupied e orbital.

The linear relationship between the chemical shift of L_3 peak of XPS and the charge on metal ion in various chromium compounds has been reported by Carver et al.[18]. They found a straight line with a slope of 2.1 eV chemical shift per unit electronic charge. By using of this relation, the chemical shift of -0.5 eV is related to the increase of charge about 0.24 electron per chromium ion in the GIC. Although this is a rough estimation, it may be concluded that all chromium ion is not reduced to the oxidation state of five, as previously proposed by Ebert et al.[8].

Finally we consider the ELNES of the oxygen K edge shown in Fig. 5. The spectrum shape and energy positions of the ELNES of the GIC is again close to that of K_2CrO_4 rather than Cr_2O_3, which is consistent with the results from the

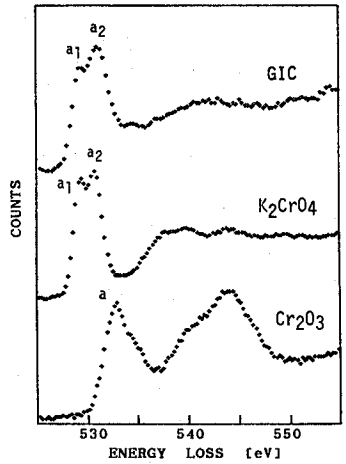

Fig. 5. The oxygen *K*-shell excitation spectra of chromium trioxide-GIC, K_2CrO_4 and Cr_2O_3. The energies of the labelled peaks are given in Table 1.

chromium *L* edge. According to the dipole selection rule, the oxygen *K* edge spectrum is related to the transition from the 1*s* level to the unoccupied molecular orbital containing the oxygen 2*p* orbital.

In the spectra of K_2CrO_4 and the GIC the main peak is split into a_1 and a_2 peaks. The energy separations between the a_1 and a_2 peaks are 1.3 eV and 1.5 eV for K_2CrO_4 and GIC, respectively, and are different from the crystal field splitting of 2.2 eV determined by the splitting of chromium L_3 peaks. In the case of oxygen *K* edge spectrum the molecular orbital approach using the $(CrO_4)^{2-}$ cluster is not adequate because the chemical environment around each oxygen ion is not equivalent. Indeed, in the crystal of K_2CrO_4[19] four oxygen surround the chromium ion keeping the equal Cr–O distances of 1.64 Å and each oxygen separates 2.68 Å from the other one. However, the arrangements of nearest neighbor potassium ions around the oxygen ion can be classified into two types. That is, one type to which three oxygen ions belong shows that the O–K distance is about 2.72 Å and the angle of Cr–O–K is about 180 degree. The other one to which one oxygen ion belongs shows that the O–K distance is 3.17 Å and the angle of Cr–O–K is about 80 degree. Such a difference of the local structure around each oxygen ion may alter the energy position of the unoccupied orbital or the binding energy of the oxygen 1*s* core electron. This may be the reason for the splitting of the oxygen peak. Therefore, for more quantitative understanding of the ELNES of oxygen *K* edge the molecular orbital calculations based on clusters representing the environment around each oxygen ion are probably necessary, but it is beyond the scope of this paper.

However, it is noticeable that no appreciable energy shift is observed between the spectra of the oxygen *K* edge of the GIC and K_2CrO_4. This fact suggests that the electronic structure around the oxygen ion is not affected by the oxidation reaction of graphite layers. Therefore, the charges transfered from graphite layers

are localized on the chromium ion.

In conclusion, by investigating the ELNES of the chromium trioxide intercalated into graphite as well as that of K_2CrO_4 and Cr_2O_3, we have determined the local structure around the chromium ion and the oxidation state of the GIC. The chromium ion in the GIC is tetrahedrally surrounded by four oxygen ions and is partially reduced to the oxidation state of five by the charge transfer from the graphite layers. These results have demonstrated the sensitivity of EELS to the local structure around a particular element in the specimen.

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